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A CONVENIENT PREPARATION OF  $B_{12}H_{12}^-$  SALTS

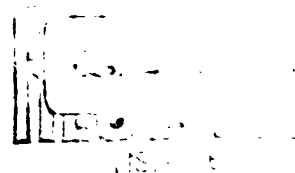
by

Ian A. Ellis, Donald F. Gaines and Riley Schaeffer.

Indiana University  
Department of Chemistry  
Bloomington, Indiana

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## A Convenient Preparation of $B_{12}H_{12}^-$ Salts.<sup>1</sup>

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1. Studies of Boranes IX. For paper VIII of this series see D. F. Gaines and R. Schaeffer, Proc. Chem. Soc., in press.
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Sir:

Studies of the  $B_{12}H_{12}^-$  anion have been severely hampered until now by the fact that it could only be prepared in poor yield from a halogenated decaborane.<sup>2</sup>

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2. A. R. Pitochelli and M. F. Hawthorne, J. Am. Chem. Soc., 82, 3228 (1960).
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The high stability of this anion and of its derivatives considered together with the versatility of its substitution reactions<sup>3</sup> make the chemistry of this

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3. W. H. Knoch, et. al., J. Am. Chem. Soc., 84, 1056 (1962).
- 

ion an intriguing area for research. We would therefore like to report a more convenient preparation of this anion from readily available starting materials by conventional techniques. At the same time this is a striking example of the formation of a highly stable end product by a quite unexpected route. Small yields of  $B_{10}H_{10}^-$  salts are produced as byproducts.

In the course of carrying out  $^{11}B$  n.m.r. spectral studies on the triborohydride anion it was found that heating a solution of  $NaB_3H_6$  in diethyleneglycol dimethyl ether (M1) for two hours on a steam bath caused the  $^{11}B$  n.m.r. spectrum to change. The multiplet arising from  $B_3H_6^-$  was completely replaced by a doublet of approximately the same overall intensity with a chemical shift of 14.6 p.p.m. and a coupling constant of 126 c.p.s. This corresponded to the values for  $B_{11}H_{14}^-$ <sup>4</sup> and  $B_{12}H_{12}^-$ <sup>3</sup> within experimental error.

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4. V. D. Aftandillian, et. al., Inorg. Chem., 1, 734 (1962).
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A freshly prepared solution of  $\text{NaB}_3\text{H}_6$  (16.5g.) in 141 prepared by in situ hydroboration of sodium borohydride<sup>5</sup> was refluxed under a nitrogen atmosphere

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5. D. F. Gaines, R. Schaeffer and F. Tebbe, *Inorg. Chem.* 2, 526 (1963).

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until colorless (16 hrs). When the resulting mixture was treated with a concentrated solution of  $(\text{CH}_3)_3\text{NHCl}$  (30g) in water an exothermic reaction occurred which was accompanied by evolution of gaseous amine. The resulting mixture was cooled to room temperature and the solid which separated was filtered and dried to yield 27 g. of crude products.

A fraction of the crude solid was dissolved in water and treated with a saturated solution of cesium chloride in water until no further precipitation took place. The precipitate was recrystallized three times from water to give a highly crystalline colorless solid. An X-ray powder diffraction pattern of this solid showed maximum reflections at  $d$  values of 3.59, 4.21, 2.16 and 2.60 and was identical to the diffraction pattern of a similar material prepared in similar fashion from an authentic sample of  $(\text{Et}_3\text{NH})_2\text{B}_{12}\text{H}_{12}$ <sup>6</sup>.

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6.  $(\text{Et}_3\text{NH})_2\text{B}_{12}\text{H}_{12}$  was kindly supplied by Professor M. F. Hawthorne.

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The remainder of the crude product was recrystallized from a water ethanol mixture to give  $(\text{Me}_3\text{NH})_2\text{B}_{12}\text{H}_{12}$  identified by its <sup>11</sup>B n.m.r. spectrum. Concentration of the mother liquor by conventional techniques gave further quantities of  $(\text{Me}_3\text{NH})_2\text{B}_{12}\text{H}_{12}$  and also in the last fractions some  $(\text{Me}_3\text{NH})_2\text{B}_{10}\text{H}_{10}$ , (identified by its <sup>11</sup>B n.m.r. spectrum)<sup>7</sup>.

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7. A. R. Pitochelli, et. al., *J. Am. Chem. Soc.*, 84, 1057 (1962).

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Yields were not definitely established since complete separation of  $(\text{Me}_3\text{NH})_2\text{B}_{12}\text{H}_{12}$  from  $(\text{Me}_3\text{NH})_2\text{B}_{10}\text{H}_{10}$  could not be readily achieved but the yield

of  $B_{12}H_{12}$  was at least 65%. The yield of  $B_{10}H_{10}$  was roughly 3%.

Thin layer chromatography carried out on the crude reaction product using silica gel and water as eluent showed that it consisted of at least three components with respective  $R_f$  values of 0, 0.3 and 1. The fraction with  $R_f 1$  was shown to be  $B_{12}H_{12}$  and  $B_{10}H_{10}$ . The other compounds present in the mixture are under investigation.

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Contribution No. 0000  
Department of Chemistry  
Indiana University  
Bloomington, Indiana

Ian A. Ellis  
Donald F. Gaines  
Riley Schaeffer